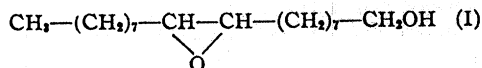


# Chemistry of Epoxy Compounds. X.<sup>1</sup> Polymerization of the Isomeric 9,10-Epoxyoctadecanols

BY DANIEL SWERN AND GERALDINE N. BILLEN

The thermal polymerization of the isomeric 9,10-epoxystearic acids was recently reported.<sup>2</sup> The present note reports the results of the thermal polymerization of the isomeric 9,10-epoxyoctadecanols (I), m. p. 54 and 48°, respectively, in



the presence of naphthalene-2-sulfonic acid as catalyst.

**Starting Materials.**—The isomeric 9,10-epoxyoctadecanols, m. p. 54 and 48°, were prepared from oleyl<sup>3</sup> and elaidyl<sup>4</sup> alcohols, respectively, by epoxidation with peracetic<sup>5</sup> or perbenzoic acid.<sup>6</sup> Calcd. for  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , oxirane oxygen,<sup>7</sup> 5.62%; found, 5.62%.

**Polymerization Procedures.**—9,10-Epoxyoctadecanol (either isomer) and the required quantity of naphthalene-2-sulfonic acid were mixed and then ground until the catalyst was uniformly distributed. Approximately 5-g. portions of the mixture were then weighed into a series of test-tubes which had been flushed with nitrogen or carbon dioxide. After being filled, the tubes were again flushed with inert gas, stoppered tightly, and then immersed in a constant-temperature oil-bath which maintained the desired temperature to  $\pm 0.2^\circ$ . Fifteen minutes was allowed for the establishment of temperature equilibrium before the polymerization time was counted. During the equilibration period, the tubes were shaken occasionally to ensure homogeneity. At selected time intervals, a tube was removed from the oil-bath, cooled rapidly to room temperature, and then analyzed within twenty-four hours.

**Analytical Procedures.**—Analyses were carried out as previously reported.<sup>2</sup> Carbonyl oxygen was determined by the procedure reported by Knight and Swern.<sup>8</sup>

## Discussion

Figure 1 shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (ol), m. p. 54°, at 60, 80, 90 and 100°. Figure 2 shows the course of the catalyzed polymerization of 9,10-epoxyoctadecanol (el), m. p. 48°, at 80, 90, 100, 120 and 140°. These data may be briefly summarized as follows: (a) under identical conditions, the high-melting epoxyoctadecanol (ol) polymerizes at a more rapid rate than does the low-melting isomer (el); (b) both isomers can be converted to viscous liquids if the polymerization is permitted to proceed far enough; (c) when the oxirane oxygen value is substantially zero, the molecular weight is about 900, or approximately that of a trimer; (d) in all the polymerizations except the one at 60°, about 20 to 30% of

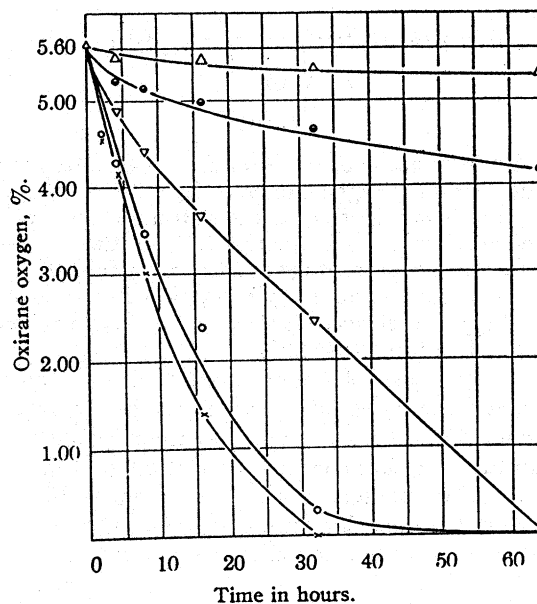


Fig. 1.—Thermal polymerization of 9,10-epoxyoctadecanol(ol), m. p. 54°, with naphthalene-2-sulfonic acid as catalyst: O, 90°, 2% catalyst; Δ, 60°, 0.75% catalyst; X, 100°, 2% catalyst; ●, 80°, 0.75% catalyst; ∇, 100°, 0.75% catalyst.

the reduction in oxirane oxygen can be accounted for by isomerization to the carbonyl group; (e) in two cases in which the comparison has been made, molecular weights determined ebulliosopi-

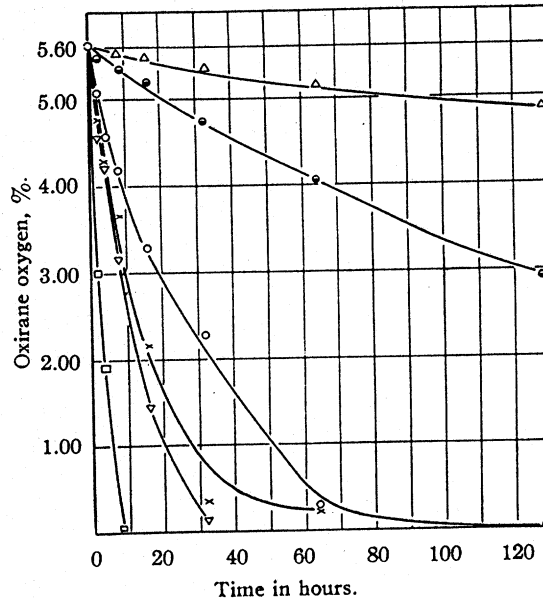


Fig. 2.—Thermal polymerization of 9,10-epoxyoctadecanol(el), m. p. 48°, with naphthalene-2-sulfonic acid as catalyst: O, 90°, 2% catalyst; Δ, 80°, 0.75% catalyst; ∇, 120°, 0.75% catalyst; X, 100°, 2% catalyst; ●, 100°, 0.75% catalyst; □, 140°, 0.75% catalyst.

(1) For the previous paper in this series, see THIS JOURNAL, 71, 2219 (1949).

(2) Swern, Billen and Eddy, THIS JOURNAL, 70, 1228 (1948).

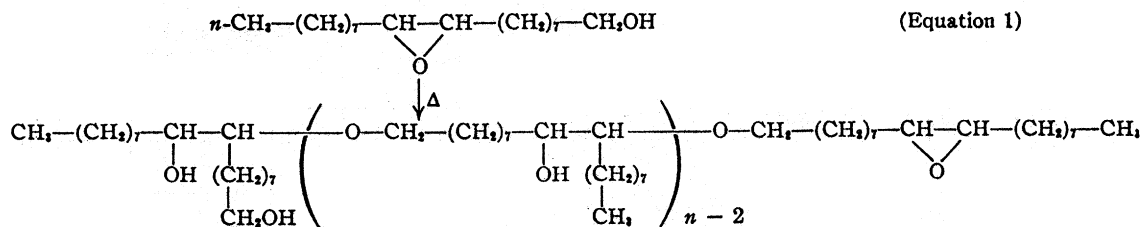
(3) Swern, Knight and Findley, *Oil and Soap*, 21, 133 (1944).

(4) Swern, Jordan and Knight, THIS JOURNAL, 68, 1673 (1946).

(5) Swern, Findley and Scanlan, *ibid.*, 66, 1925 (1944).

(6) Findley, Swern and Scanlan, *ibid.*, 67, 412 (1945).

(7) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, 19, 414 (1947); Nicolet and Poulter, THIS JOURNAL, 52, 1186 (1930).



(Equation 1)

cally in benzene differ from those calculated from the oxirane oxygen analyses by only 7 to 15%; (f) the isomerization of the oxirane group to the carbonyl group is a function of both the temperature and the percentage of catalyst, although there appears to be no simple relationship involved; and (g) the refractive index of the polymers levels off at 1.462 to 1.464 (60°).

On the basis of the data reported here and the known reactions of oxirane groups, it can be concluded that the main reactions which occur during the thermal polymerization of the 9,10-epoxyoctadecanols are (a) a condensation reaction between the oxirane and primary hydroxyl groups, yielding a polyether, as shown in Equation

I, and (b) isomerization of the oxirane group to the carbonyl group. All the polymers are readily soluble in the common organic solvents, with the exception of petroleum naphtha, thus indicating that cross-linking reactions occur only to a limited extent, if at all.

No information is available on the occurrence of other possible acid-catalyzed condensation and addition reactions, such as dioxane or polyethylene oxide formation.<sup>2</sup>

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(8) Knight and Swern, *J. Am. Oil Chem. Soc.*, **36**, 366 (1949).

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